INFLUENCE OF STERIC CONFIGURATION ON THE ABSORPTION SPECTRA OF α-DIKETONES

BY

PAUL MILLER MADER

B.S., California Institute of Technology, 1942

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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IN THE GRADUATE COLLEGE OF THE
UNIVERSITY OF ILLINOIS, 1950

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R. UNIV. BIBLIOTHEEK LEIDEN

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Introduction

The apparent absence of a dicarbonyl absorption band in the ultraviolet spectra of benzil and certain substituted benzils has been ascribed to noncoplanarity of the carbonyl groups (1). It was of interest, in this connection, to determine experimentally the relation between the steric configuration of the dicarbonyl system and its action as a chromophore.

Purely aliphatic 1,2-diketones were chosen for this study, and it was proposed to regulate the relative orientation of the carbonyl groups by inclusion of the dicarbonyl system in cyclic structures. Studies of glyoxal and biacetyl (2) indicate that the carbonyl groups of acyclic 1,2-diketones tend to assume a *trans* orientation. In cyclic 1,2-diketones, on the other hand, the dicarbonyl system can be restricted to a configuration approaching pure *cis* as the ring size is reduced.

All chance for enolization in the cyclic ketones had to be eliminated, since in the case of the smaller rings, at least, cyclic 1,2-diketones exist largely as the monoenols (3).

Discussion Of Results

The following 1,2-diketones were prepared and their ultraviolet absorption spectra determined: camphorquinone, 3,3,6,6-tetramethyl-1,2-cyclohexanedione, 3,3,7,7-tetramethyl-1,2-cycloheptanedione, 3,3,8,8-tetramethyl-1,2-cycloöctanedione (not obtained in a pure state), 3,3,18,18-tetramethyl-1,2-cycloöctadecanedione, and dipivaloyl (2,2,5,5-tetramethyl-3,4-hexanedione).

The absorption spectra of these compounds are characterized by two bands in the 230 to 500 mμ region. The long wave length band, presumedly uniquely associated with the 1,2-dicarbonyl system, shifts its position in a marked and

regular manner as the relative orientation of the carbonyl groups[1] is altered. This band moves toward shorter wave lengths as the carbonyl groups diverge from a *cis* configuration, reaching a position of minimum wave length when the carbonyl groups lie in planes at about right angles to each other, and then it returns to longer wave lengths as the carbonyl groups approach *trans* orientation. The short wave length band, perhaps arising from activation of the carbonyl groups individually, does not change its position markedly as the relative orientation of the carbonyl groups is changed.

The observed changes in the position of the long wave length absorption band can be explained on the basis of a decrease in stability of the activated form of the dicarbonyl system as the carbonyl groups depart from coplanarity. If, as has been supposed, the activated form is characterized by a carbon-carbon bond possessing a significant amount of double bond character, then, indeed, twisting the carbonyl groups out of coplanarity should increase the energy of the activated form.

All of the diketones studied, except camphorquinone, were prepared by chromic anhydride oxidation of the corresponding acyloins, which, in turn, were synthesized by known techniques (4) starting with the appropriate esters. The carboxylic acids from which the esters were derived were synthesized by the Kolbe electrolysis in the case of 1,1,4,4-tetramethyladipic acid (5) and by the method of Haller and Bauer (6) in the case of the other dibasic acids. In several instances the techniques used to carry out these reactions were simplified and altered so as to give higher yields than previously realized. Pivalic acid, already on hand, had been prepared by the reaction between carbon dioxide and the Grignard reagent derived from *tert*-butyl chloride. Camphorquinone was obtained by selenium dioxide oxidation of camphor as described by Evans, Ridgion, and Simonsen (7).

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1. The configurations of the dicarbonyl system were estimated with the aid of Fisher-Hirschfelder-Taylor molecular models of the compounds studied.

During the synthesis of the cyclic acyloin, 3,3,8,8-tetramethyl-2-hydroxycycloöctanone, a by-product was formed which is believed to have been 2,2,7,7-tetramethylcycloöctanol. This alcohol was oxidized to the corresponding ketone.

Quinoxalines were prepared from camphorquinone (8), 3,3,6,6-tetramethyl-1,2-cyclohexanedione, and 3,3,7,7-tetramethyl-1,2-cycloheptanedione, and their ultraviolet absorption spectra were determined. The spectra are all very much alike, perhaps supporting the theory that large differences in the spectra of the diketones arise as a result of variations in the steric configuration of the dicarbonyl system.

The ultraviolet absorption spectrum of 2,2′-dimethylbenzil was determined in connection with a proposed study of benzils possessing a methylene bridge between *ortho* positions of the two aromatic rings.

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VITA

The author was born in Boise, Idaho, on May 9, 1920. He received his elementary education in the public schools of Los Angeles, California, and his secondary education at Fairfax High School, Los Angeles, California, from which he was graduated in 1938. After having attended the California Institute of Technology, where he received the Bachelor of Science Degree in Chemistry in the spring of 1942, he spent four years as a research chemist with the Naugatuck Chemical Division of the United States Rubber Company, Naugatuck, Connecticut. In the fall of 1946 he entered the Graduate School of the University of Illinois, where he has held second- and third-year University Fellowships.